Nonlinear dielectric relaxation of polar molecules in a strong ac electric field: Steady state response

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The nonlinear dielectric relaxation ac stationary response of an assembly of rigid polar molecules acted on by strong superimposed external dc $\mathbf{E}_0$ and ac $\mathbf{E}_1(t)=\mathbf{E}_1\cos\omega t$ electric fields is evaluated in the context of the noninertial rotational diffusion model. The calculation proceeds by expanding the relaxation functions $f_n(t)$ (the expectation value of the Legendre polynomials P_n), which describe the nonlinear relaxation of the system, as a Fourier series in the time domain. Hence, an infinite hierarchy of recurrence equations for the Fourier components of $f_n(t)$ is obtained. The exact solution of this hierarchy can be obtained in terms of a matrix continued fraction, so allowing us to evaluate the ac nonlinear response. For a weak ac field our results are in complete agreement with previous solutions obtained by perturbation methods. Diagrams showing the behavior of the in-phase and out-of-phase components of the electric polarization are presented.

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I. INTRODUCTION

The theory of electric polarization of dielectric fluids plays an essential role in our understanding of electrooptical relaxation phenomena. Originally this problem was treated by Debye [1] who calculated the linear dielectric response of polar molecules to a weak ac electric field in the context of the noninertial rotational diffusion model. This linear response has the well-known representation in terms of the Debye equations for the complex dielectric susceptibility and of the Cole-Cole diagrams, which are perfect semicircles. The linear susceptibility is independent of the electric field strength **E**. Several theoretical approaches have been proposed to generalize the Debye theory in order to take into account nonlinear effects of dielectric relaxation of polar fluids in high electric fields, see for example Refs. [2–8], and references cited therein. These approaches usually commence with the noninertial Langevin equation for the rotational Brownian motion of a particle or with the corresponding Smoluchowski equation for the probability distribution function W of orientations of the particles in configuration space. The Smoluchowski equation can be solved, for example, by expanding W in terms of a complete set of appropriate functions, usually as a series of spherical harmonics $Y_{l,m}$. This yields an infinite hierarchy of differential-recurrence relations for the moments—the expectation values of the spherical harmonics $\langle Y_{l,m}\rangle(t)$. [The underlying Langevin equation can also be reduced to this moment system (without recourse to the Smoluchowski equation) by means of an appropriate transformation of the variables and by direct averaging of the stochastic equation so obtained [9].] Approximate solutions of this hierarchy have hitherto only been obtained by using various perturbation methods in the approximation when the energy of the dipolar molecule in the external ac field is (much) less than the thermal energy kT. Furthermore, Morita [10] and Morita and Watanabe [11] proposed a general formal theory of nonlinear response arising from the transient and stationary processes for systems which dynamics is governed by the Smoluchowski equation. However, this theory is very difficult to apply to relaxation problems in the presence of an ac field of arbitrary strength due to mathematical difficulties encountered. Indeed, the only application of the theory given in Ref. [11] was an evaluation of the birefringence for a weak ac field superimposed on a weak dc bias field. Thus, the problem of the calculation of the nonlinear response in high ac fields, where the perturbation approaches are inapplicable, still remains unsolved. On the other hand, in recent papers [12–14] we have been able to calculate the *nonlinear response* for the rise, decay and rapidly rotating field transient dielectric relaxation arising from sudden changes both in magnitude and in direction of a strong external dc field. In order to obtain these results, we have used the approach developed in Refs. [15] and [16] for the solution of infinite hierarchies of *multiterm* recurrence equations. This approach is based on the matrix continued fraction technique and essentially constitutes a further development of Risken's continued fraction method [17]. In the present paper we shall show how this approach can also be applied to the calculation of the nonlinear ac stationary response of rigid polar molecules to an ac field of arbitrary strength. This approach is, in some respects, analogous to those used in Ref. [18] for the calculation of the harmonic mixing in a cosine potential and in Ref. [19] for the evaluation of the mean beat frequency of the dithered-ring-laser gyroscope. However, the model used here and the solution so obtained differ from those of Refs. [18] and [19]. Moreover, our solution has the merit of being considerably simpler than those previously available.

II. GENERAL RELATIONS

We shall consider the nonlinear dielectric relaxation of an assembly of rigid polar symmetric top particles (macromolecules) dissolved in a nonpolar solvent and acted on by strong external superimposed dc $\mathbf{E}_0$ and ac $\mathbf{E}_1(t)=\mathbf{E}_1\cos\omega t$ electric fields. Each particle contains a rigid electric dipole $\boldsymbol{\mu}$ directed along the axis of symmetry. Let us also suppose for simplicity that both $\mathbf{E}_0$ and $\mathbf{E}_1$ are directed along the Z axis of the laboratory coordinate system and that effects due to the anisotropy of the polarizability of the particles can be neglected. Then the noninertial rotational Brownian motion of the particles may be described by the

Smoluchowski equation for the probability distribution function $W(\vartheta,t)$ of the orientations of the dipoles in configuration space [1,2]

$$2\tau_D\frac{\partial}{\partial t}W(\vartheta,t)=\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial}{\partial\vartheta}W(\vartheta,t)+\frac{W(\vartheta,t)}{kT}\frac{\partial}{\partial\vartheta}V(\vartheta,t)\right)\right], \tag{1}$$

where ϑ is the angle between the axis of symmetry of the molecule and the Z axis of the laboratory coordinate system, τ_D is the usual Debye relaxation time,

$$V(\vartheta,t)=-\mu[E_0+E_1(t)]\cos\vartheta \tag{2}$$

is the orientational potential energy of the molecule, k is the Boltzmann constant, T is the temperature, and μ is the permanent dipole moment. The problem we want to solve is intrinsically nonlinear because we assume that the magnitudes of both ac and dc fields are large enough so that the energy of the molecule in these fields may be comparable or higher than kT.

On expanding $W(\vartheta,t)$ as a series of Legendre polynomials $P_n(\cos\vartheta)$ and using Eq. (1), one can obtain the following set of differential-recurrence equations (e.g., Refs. [1,2]):

$$\tau_D\frac{d}{dt}f_n(t)+\frac{n(n+1)}{2}f_n(t)=\zeta(t)\frac{n(n+1)}{2(2n+1)}[f_{n-1}(t)-f_{n+1}(t)], \tag{3}$$

where $f_n(t)$ denotes the expectation value of the Legendre polynomial of order n, namely,

$$f_n(t)=\langle P_n(\cos\vartheta)\rangle(t)=\int_0^\pi P_n(\cos\vartheta)W(\vartheta,t)\sin\vartheta\,d\vartheta, \tag{4}$$

and $\zeta(t)$ is a dimensionless field parameter which may be separated into two parts as follows:

$$\zeta(t)=\xi_0+\xi\cos\omega t, \tag{5}$$

$$\xi_0=\frac{\mu E_0}{kT},\quad \xi=\frac{\mu E_1}{kT}. \tag{6}$$

We note that Eq. (3) has also been derived in Refs. [9,12,14] directly from the underlying vector Euler-Langevin equation in the noninertial limit.

Our goal is to evaluate the ac stationary response of the electric polarization $P(t)$ [1,2], which is defined as

$$P(t)=\mu N_0\langle\cos\theta\rangle(t)=\mu N_0 f_1(t), \tag{7}$$

where N_0 is the concentration of polar molecules. Here the internal field effects are not taken into account. This means that the effects of long-range torques due to the connection between the average moments and the Maxwell fields are not taken into account. A treatment of these effects for the static nonlinear dielectric increment has been given by Fulton [20]. However, for the ac nonlinear response, the account of the internal field effects is a very difficult problem. Nevertheless, this problem may be ignored for electrically diluted systems in first approximation.

III. MATRIX CONTINUED FRACTION SOLUTION OF EQ. (3)

Since we are solely concerned with the ac response corresponding to the stationary state, which is independent of the initial conditions, we may seek all the $f_n(t)$ in the form of a Fourier series, viz.,

$$f_n(t)=\sum_{k=-\infty}^{\infty}F_k^n(\omega)e^{ik\omega t}. \tag{8}$$

As all the $f_n(t)$ are real, the Fourier amplitudes F_k^n must satisfy the following condition:

$$F_{-k}^n=(F_k^n)^*, \tag{9}$$

where the asterisk denotes the complex conjugate.

On substituting Eq. (8) into Eq. (3), we have the following recurrence relations for the Fourier amplitudes $F_k^n(\omega)$, namely:

$$z_{n,k}(\omega)F_k^n(\omega)-2\xi_0[F_k^{n-1}(\omega)-F_k^{n+1}(\omega)]-\xi[F_{k-1}^{n-1}(\omega)+F_{k+1}^{n-1}(\omega)-F_{k-1}^{n+1}(\omega)-F_{k+1}^{n+1}(\omega)]=0, \tag{10}$$

where

$$z_{n,k}(\omega)=2(2n+1)\left[1+\frac{2i\omega\tau_D k}{n(n+1)}\right]. \tag{11}$$

The solution of Eq. (10) can be obtained in terms of matrix continued fractions as follows. Let us introduce the column vectors $\mathbf{C}_n(\omega)$ and $\mathbf{R}$:

$$\mathbf{C}_n(\omega)=\begin{pmatrix}\vdots\\ F_{-2}^n(\omega)\\ F_{-1}^n(\omega)\\ F_0^n(\omega)\\ F_1^n(\omega)\\ F_2^n(\omega)\\ \vdots\end{pmatrix}\quad\text{and}\quad\mathbf{R}=\begin{pmatrix}\vdots\\ 0\\ \xi\\ 2\xi_0\\ \xi\\ 0\\ \vdots\end{pmatrix}.$$

[As is obvious from its definition, the vector $\mathbf{C}_1$ contains all the Fourier amplitudes of $f_1(t)$, which are necessary for obtaining the ac nonlinear dielectric response.] Then the *seven-term* recurrence Eq. (10) can be transformed into the *matrix three-term* recurrence equations

$$\mathbf{Q}_1(\omega)\mathbf{C}_1(\omega)+\mathbf{q}\mathbf{C}_2(\omega)=\mathbf{R}, \tag{12}$$

$$\mathbf{Q}_n(\omega)\mathbf{C}_n(\omega)+\mathbf{q}\mathbf{C}_{n+1}(\omega)=\mathbf{q}\mathbf{C}_{n-1}(\omega),\quad n=2,3,..., \tag{13}$$

where $\mathbf{q}$ and $\mathbf{Q}_n(\omega)$ are tridiagonal and diagonal infinite matrices, respectively, defined as

$$\mathbf{q}=\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \iddots \\ \cdots & 2\xi_0 & \xi & 0 & 0 & 0 & \cdots \\ \cdots & \xi & 2\xi_0 & \xi & 0 & 0 & \cdots \\ \cdots & 0 & \xi & 2\xi_0 & \xi & 0 & \cdots \\ \cdots & 0 & 0 & \xi & 2\xi_0 & \xi & \cdots \\ \cdots & 0 & 0 & 0 & \xi & 2\xi_0 & \cdots \\ \iddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{14}$$

and

$$\mathbf{Q}_n(\omega)=\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \iddots \\ \cdots & z_{n,-2}(\omega) & 0 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & z_{n,-1}(\omega) & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & z_{n,0}(\omega) & 0 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & z_{n,1}(\omega) & 0 & \cdots \\ \cdots & 0 & 0 & 0 & 0 & z_{n,2}(\omega) & \cdots \\ \iddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \tag{15}$$

where $z_{n,k}(\omega)$ is given by Eq. (11).

Insofar as we are interested in the determination of $\mathbf{C}_1(\omega)$ only, the infinite system of Eqs. (12) and (13) can readily be solved in terms of matrix continued fractions [16,17]. Thus, we obtain

$$\mathbf{C}_1(\omega)=\mathbf{S}(\omega)\mathbf{R}, \tag{16}$$

where the infinite matrix continued fraction $\mathbf{S}$ is given by

$$\mathbf{S}(\omega)=\cfrac{\mathbf{I}}{\mathbf{Q}_1(\omega)+\mathbf{q}\cfrac{\mathbf{I}}{\mathbf{Q}_2(\omega)+\mathbf{q}\cfrac{\mathbf{I}}{\mathbf{Q}_3(\omega)+\cdots}\mathbf{q}}\mathbf{q}} \tag{17}$$

(the fraction lines designate the matrix inversions) and $\mathbf{I}$ is the identity matrix of infinite dimension.

Having determined the column vector $\mathbf{C}_1(\omega)$ from Eq. (16), one can calculate the stationary ac response function $f_1(t)$, which may be presented as follows:

$$f_1(t)=F_0^1(\omega)+2\sum_{k=1}^{\infty}\ \mathrm{Re}\{F_k^1(\omega)e^{ik\omega t}\}. \tag{18}$$

The $F_0^1(\omega)$ in the right hand side of Eq. (18) is a time independent, but frequency dependent term. This frequency dependence is due to the coupling effect of the dc bias $\mathbf{E}_0$ and ac $\mathbf{E}_1(t)$ fields. In the absence of the dc bias field, i.e., for $\xi_0=0$, the series (18) contains only the odd components of F_k^n (all the even components are equal to zero) and reduces to

$$f_1(t)=2\sum_{k=1}^{\infty}\ \mathrm{Re}\{F_{2k-1}^1(\omega)e^{i(2k-1)\omega t}\}. \tag{19}$$

IV. RESULTS AND DISCUSSION

The *exact* matrix continued fraction solution [Eqs. (16) and (17)] we have obtained is very convenient for the purpose of computation (various algorithms for calculating matrix continued fractions are discussed in Ref. [17] Chap. 9). As far as the calculation of the infinite matrix continued fraction $\mathbf{S}$ is concerned, we approximated it by some matrix continued fraction of finite order (by putting $\mathbf{Q}_n=\mathbf{0}$ at some $n=N$). At the same time we confined the dimensions of the matrices $\mathbf{Q}_n$ and $\mathbf{q}$ to some finite number M. Both N and M depend on the field parameters ξ, ξ_0 and on the number of harmonics to be determined. They must be chosen taking account of the desired degree of accuracy of the calculation. For example, for the calculation of $F_k^1(\omega)$ up to $k=7$ and for ξ and ξ_0 up to 20, the dimension of $\mathbf{Q}_n$ and $\mathbf{q}$ need not exceed 50 and 15–20 iterations in calculating $\mathbf{S}$ are enough to arrive at an accuracy of not less than six significant digits in the majority of cases.

Let us first of all consider main features of the ac nonlinear response in the absence of the dc bias field, i.e., for $\xi_0=0$. The low ($\omega\to 0$) and high ($\omega\to\infty$) frequency asymptotic behavior of the Fourier components $F_k^1(\omega)$ may be evaluated from the recurrence relation (10). These asymptotic estimates for $F_k^1(\omega)$ at $k=1$, 3, 5, and 7 are summarized in Table I. Equations for the low frequency behavior of $F_k^1(\omega)$ presented in Table I were obtained by using the perturbation expansion of $F_k^1(\omega)$ in powers of ξ so that they are valid for $\xi\ll 1$ only. The high frequency asymptotic expansions of $F_k^1(\omega)$ were derived by assuming arbitrary ξ, thus they are applicable to any ξ. This may be explained by the fact that in the limit $\omega\to\infty$ the dipole polarization plays no role as the dipoles are ''frozen'' due to viscosity of the solution and they have no time to follow the changes of the ac field independently of the strength of the ac field.

The results of the calculation of the real and imaginary parts of the normalized nonlinear harmonic components of the electric polarization varying in ω, 3ω, and 5ω, viz.,

$$\chi_1^1(\omega)=6F_1^{1*}(\omega)/\xi, \chi_3^1(\omega)=360F_3^{1*}(\omega)/\xi^3,$$

and

TABLE I. The low and high frequency behavior of the Fourier components $F_n^k(\omega)$ for $\xi=0$.

	$\omega\tau_D \ll 1,\ \xi \ll 1$	$\omega\tau_D \to \infty,\ \xi$ any
$F^1_{-1}=(F^1_1)^*$	$\approx \frac{\xi}{6}[1+i\omega\tau_D+O(\omega^2\tau_D^2)]+O(\xi^3)$	$\sim \frac{\xi}{6\omega^2\tau_D^2}(1+i\omega\tau_D)$
$F^1_{-3}=(F^1_3)^*$	$\approx -\frac{\xi^3}{360}\left(1+\frac{14}{3}i\omega\tau_D+O(\omega^2\tau_D^2)\right)+O(\xi^5)$	$\sim \frac{\xi^3}{720\omega^4\tau_D^4}\left(\frac{17}{6}+i\omega\tau_D\right)$
$F^1_{-5}=(F^1_5)^*$	$\approx \frac{\xi^5}{15\,120}\left(1+\frac{41}{4}i\omega\tau_D+O(\omega^2\tau_D^2)\right)+O(\xi^7)$	$\sim \frac{\xi^5}{80\,640\omega^6\tau_D^6}\left(\frac{299}{60}+i\omega\tau_D\right)$
$F^1_{-7}=(F^1_7)^*$	$\approx -\frac{\xi^7}{604\,800}\left(1+\frac{266}{15}i\omega\tau_D+O(\omega^2\tau_D^2)\right)+O(\xi^9)$	$\sim \frac{\xi^7}{9\,676\,800\omega^8\tau_D^8}\left(\frac{3179}{420}+i\omega\tau_D\right)$

$$\chi_5^1(\omega)=15\,120F_5^{1*}(\omega)/\xi^5$$

are presented in Figs. 1–6. (The normalization was chosen in order to satisfy the condition $|\chi_n^1(0)|=1$ at $\xi\to 0$.) The spectra of $\mathrm{Re}\{\chi_1^1(\omega)\}$ (dispersion) and $\mathrm{Im}\{\chi_1^1(\omega)\}$ (absorption) and the corresponding Cole-Cole diagram of the first harmonic component are shown in Figs. 1 and 2. Here it is clearly seen how the relaxation spectrum of $\chi_1^1(\omega)$ at $\xi\ll 1$ (linear response) is transformed to the nonlinear response spectrum in high fields: with increasing of ξ the absorption and dispersion curves are shifted to higher frequencies with decreasing of the amplitude due to the saturation. A saturation level seems to be reached at $\xi\sim 5$, where all the Fourier components $F_k^1(\omega)$ become comparable in the order of magnitude (see Table I). Moreover, one can note that the half-width of the spectra $\mathrm{Im}\{\chi_1^1(\omega)\}$ enlarges (Fig. 1) as ξ increases. Defining the phase angle θ_1 between in-phase and out-of-phase components of $\chi_1^1(\omega)$ as

$$\theta_1=\tan^{-1}(\mathrm{Im}\{\chi_1^1(\omega)\}/\mathrm{Re}\{\chi_1^1(\omega)\}),$$

one can remark (Fig. 2) that the asymptotic limit of $\theta_1(\omega\to\infty)$ is equal to $\pi/2$ regardless of the value of ξ. This is so because neither the polarizability nor the inertia of the molecules was taken into account here. The account of the induced moment and the inertia effect contributions to the response may lead to different behavior of θ_1. The frequency behavior of the third harmonic component $\chi_3^1(\omega)$ is shown in Figs. 3 and 4. For $\xi\ll 1$, the real part of the 3ω component (Fig. 3) starts from -1 at low frequencies, then reaches a positive maximum at $\omega\tau_D\approx 0.77$ before decreasing monotonically to 0 when ω tends to ∞. The spectrum becomes more and more flattened as ξ increases. The imaginary part of the 3ω component (Fig. 4) passes through a negative minimum at $\omega\tau_D\approx 0.26$ for $\xi\ll 1$. This minimum is shifted to higher frequencies and its absolute value decreases with increasing ξ. An analogous behavior in the frequency domain (as that presented for the harmonic of rank 3) can be observed for $\chi_5^1(\omega)$ (fifth harmonic) with the exception that now both the real and imaginary parts are positive. As expected, the increasing of the ac field strength results in the saturation of all the Fourier components considered. All higher harmonics may be investigated in a similar way.

At small ac fields ($\xi\leqslant 0.5$) and at $\xi_0=0$, the results of our calculations are in full agreement with the perturbation solution for the first and third harmonics previously obtained by Coffey and Paranjape [2], viz.,

$$\chi_1^1(\omega)=\frac{1+i\omega\tau_D}{1+\omega^2\tau_D^2}-\xi^2\frac{27-13\omega^2\tau_D^2+i\omega\tau_D(42+2\omega^2\tau_D^2)}{60(1+\omega^2\tau_D^2)(9+4\omega^2\tau_D^2)}+O(\xi^4), \tag{20}$$

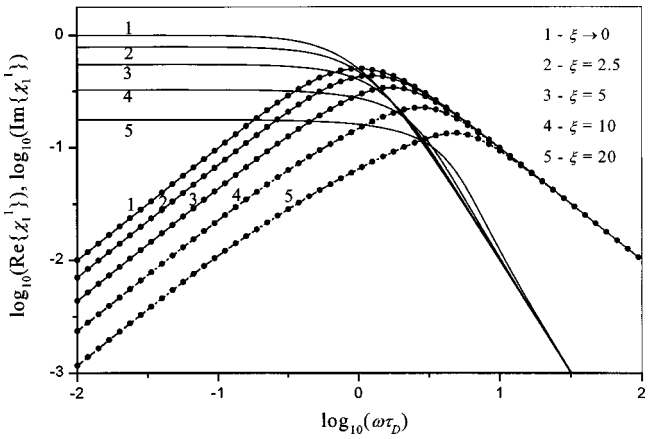

FIG. 1. $\log_{10}\mathrm{Re}\{\chi_1^1(\omega)\}$ (solid lines) and $\log_{10}\mathrm{Im}\{\chi_1^1(\omega)\}$ (filled circles) as a function of $\log_{10}(\omega\tau_D)$ for various values of ξ. Curves 1 correspond to the linear response. Note that all the curves merge in a single asymptote in the high frequency region ($\omega\to\infty$).

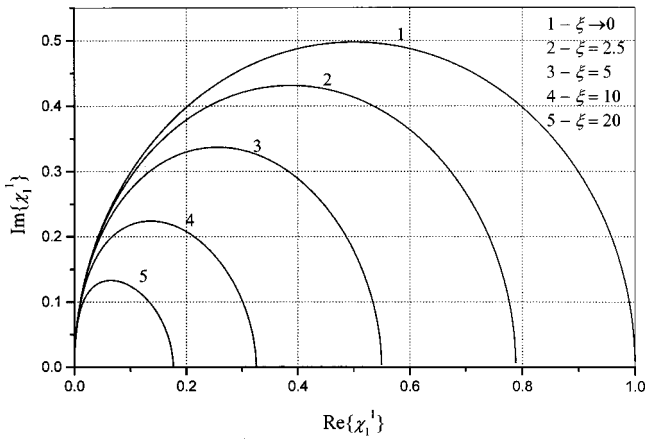

FIG. 2. Cole-Cole diagram for $\chi_1^1(\omega)$ at various values of ξ. Curve 1 (semicircle) corresponds to the linear response.

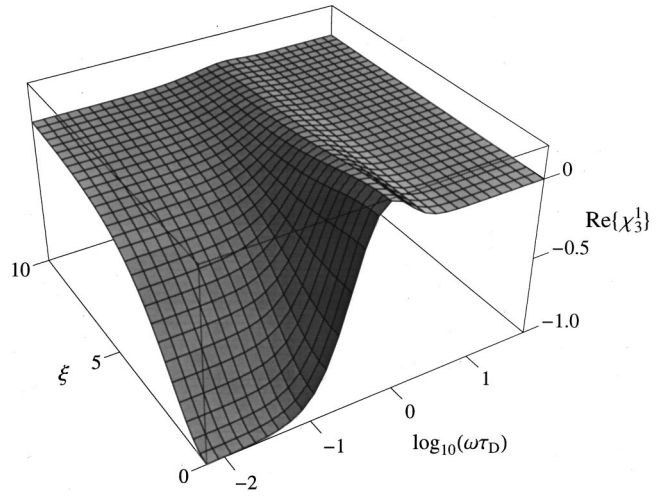

FIG. 3. Re$\{\chi_3^1\}$ (third harmonic component) as a function of $\log_{10}(\omega\tau_D)$ and ξ.

$$\chi_3^1(\omega) = -3\,\frac{3-17\omega^2\tau_D^2+i\omega\tau_D(14-6\omega^2\tau_D^2)}{(1+\omega^2\tau_D^2)(9+4\omega^2\tau_D^2)(1+9\omega^2\tau_D^2)}+O(\xi^2). \tag{21}$$

One can readily see that the asymptotic estimates for $F_1^1(\omega)$ and $F_3^1(\omega)$ presented in Table I agree in all respects with Eqs. (20) and (21). For $\xi_0 \neq 0$ similar, but more complicated equations have also been derived in Ref. [2] and later have been extended in Refs. [3–6] in order to take into account higher perturbation expansion terms.

In order to demonstrate how the dc bias field $\mathbf{E}_0$ affects the ac nonlinear response, we present here, as an example, the first harmonic component $\chi_1^1(\omega)$ as a function of the bias field parameter ξ_0. The main features of this dc bias field effect are shown in Figs. 7 and 8, where the real and imaginary parts of $\chi_1^1(\omega)$ are plotted as functions of ξ and ξ_0 for $\omega\tau_D = 1$, and in Figs. 9 and 10, where the spectra of Re$\{\chi_1^1\}$ and Im$\{\chi_1^1\}$ are presented for $0 \leqslant \xi_0 \leqslant 10$ and $\xi = 5$. As one can see in these figures, the nonlinear effects arising from the increasing of the amplitude ξ of the ac field coupled with the dc bias field $\mathbf{E}_0$ are very similar to those when $\mathbf{E}_0$ is set equal

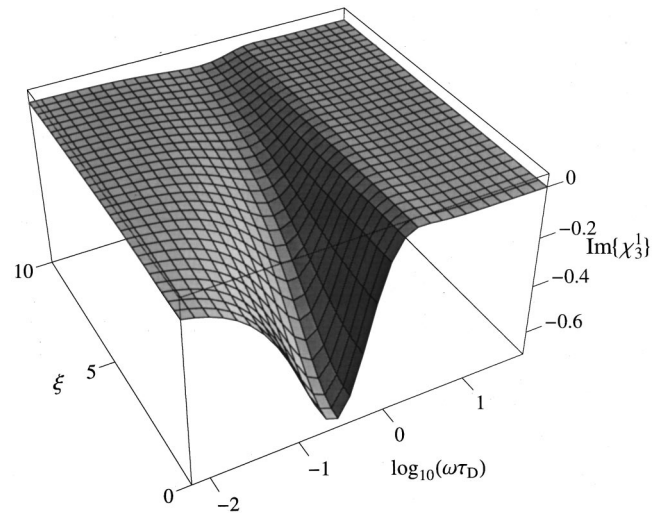

FIG. 4. The same as in Fig. 3 for Im$\{\chi_3^1\}$.

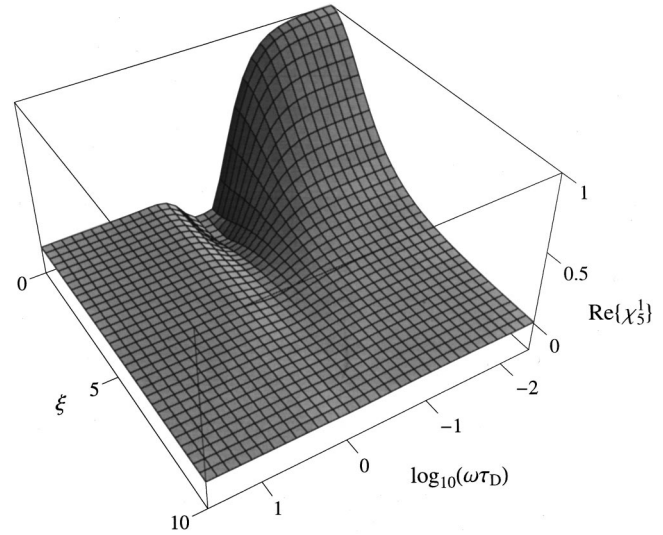

FIG. 5. Re$\{\chi_5^1\}$ (fifth harmonic component) as a function of $\log_{10}(\omega\tau_D)$ and ξ.

to zero (cf. Figs. 1 and 2). However, the increase of the bias field parameter ξ_0 results in a further decrease of the response and in its shift to higher frequencies. The half-width of Im$\{\chi_1^1\}$ enlarges with increasing ξ_0 as well. One can also see in Figs. 7–10 that the decrease of Re$\{\chi_1^1\}$ and Im$\{\chi_1^1\}$ with increasing the amplitude of the dc bias field is in several times more than that due to the ac field. For a small ac field ($\xi \ll 1$) superimposed to a strong dc bias field ($\xi_0 \gg 1$), our results are in complete agreement with those of Ref. [8], where the ac nonlinear response has been investigated by using the perturbation approach. The above conclusions in relation with these dc field effects can also be applied to higher harmonics.

In conclusion, the present theory may be applied to the interpretation of experimental data on nonlinear dielectric relaxation. We remark that until now two kinds of nonlinear response experiments have been carried out, namely, where (i) either a strong ac field alone (for example, Refs. [21,22]) or (ii) a weak ac field superimposed on a strong dc bias field (e.g., Refs. [23–25]) were applied to the dielectric liquids.

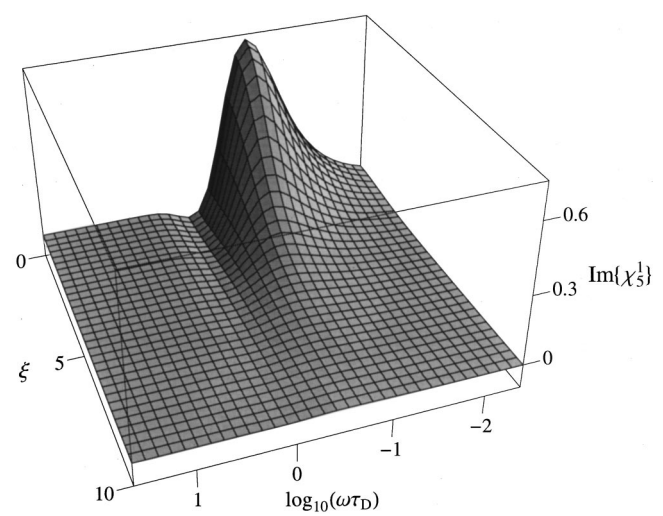

FIG. 6. The same as in Fig. 3 for Im$\{\chi_5^1\}$.

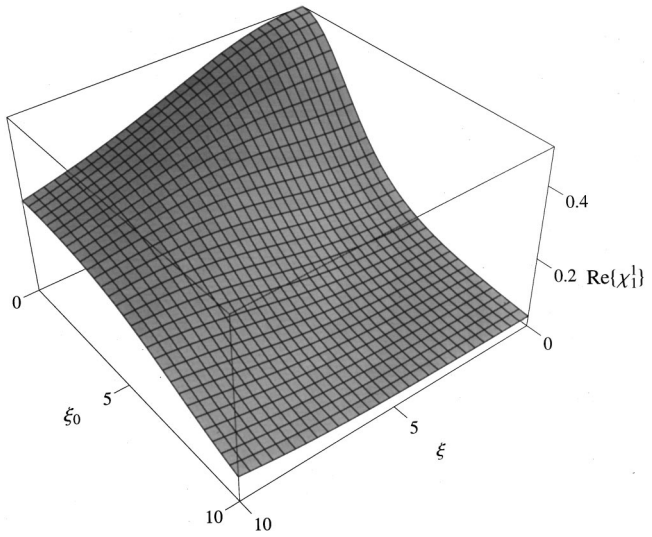

FIG. 7. Re$\{\chi_1^1\}$ as a function of ξ and ξ_0 for $\omega\tau_D=1$.

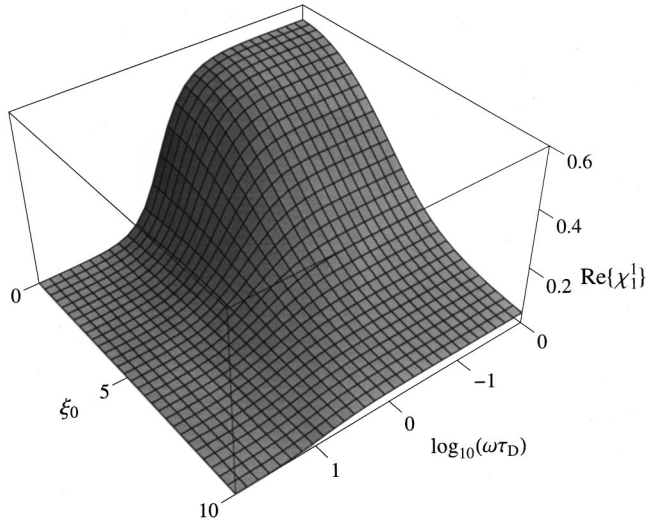

FIG. 9. Re$\{\chi_1^1\}$ as a function of $\log_{10}(\omega\tau_D)$ and ξ_0 for $\xi=5$ (strong nonlinear regime).

Although the applied fields in these experiments were high enough ($\geqslant 10^6$ V/m) to observe nonlinear effects, the strengths of the fields were still weak to allow one to use the nonlinear response equations obtained in the context of the perturbation approach. Comparison of the experimental data with the results of the perturbation theory [2–5] has demonstrated [23,24,26] that they are in agreement. Thus, the results predicted by the theory developed here are also in accordance with those experimental data. As the theory presented is applicable to arbitrary ac field strengths, it also provides a theoretical basis for comparison with nonlinear response experiments in high fields, where the perturbation methods are no longer valid. It should be noted that some molecular dynamics simulation data for systems of dipolar molecules in strong ac fields are also available (e.g., Ref. [27]). The use of computer experiment data is preferable for testing a nonlinear theory as it is much easier (than in real experiments) to achieve values of the nonlinear parameter $\xi\geqslant 1$. For example, Evans [27] reported the computer simulation data on the orientational relaxation of dipolar molecules in a strong ac field at $\xi=12$. Unfortunately, these data were only obtained for the short (picosecond) time scale, which corresponds to the frequency range, where the model under consideration is not applicable (it is valid in the low frequency region only, $\omega\tau_D\leqslant 1$) as inertial effects are ignored. In order to take into account the inertia of the molecules and to extend the area of the applicability of the theory to higher frequencies one should consider the inertial Fokker-Planck equation for the rotational Brownian motion in phase space. This will allow us to consider the nonlinear effect in the whole frequency range of dipolar polarization (up to $\sim$5 THz). We are going to extend our approach in that direction elsewhere.

Thus, in the context of the noninertial rotational diffusion model the steady state ac nonlinear response of an ensemble of rigid polar molecules in strong superimposed ac and dc bias fields can be evaluated from Eqs. (16) and (17) in terms of a matrix continued fraction. The method of the solution of infinite hierarchies of *multiterm* recurrence relations based on matrix continued fractions, which we have presented, is quite general and can also be used for calculating stationary solutions of analogous nonlinear response problems, where

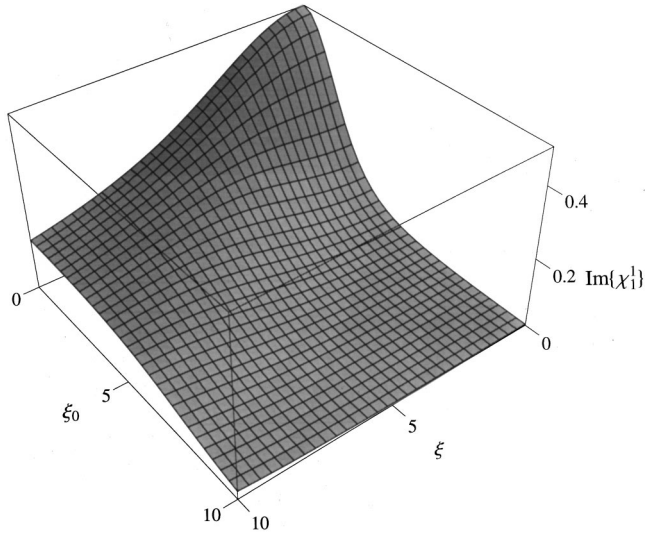

FIG. 8. The same as in Fig. 7 for Im$\{\chi_1^1\}$.

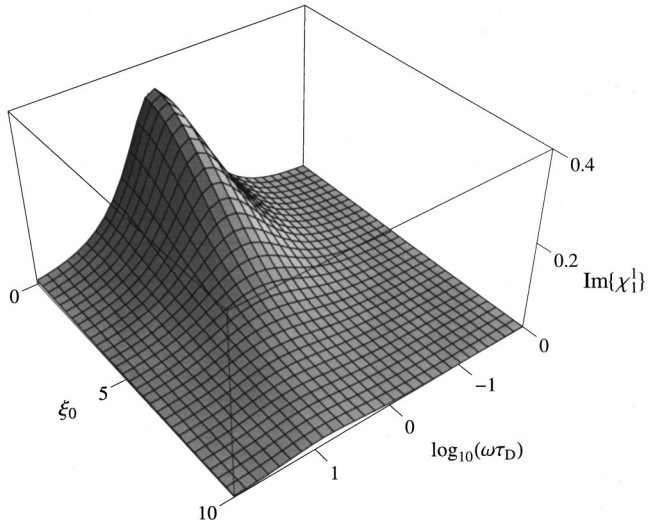

FIG. 10. The same as in Fig. 9 for Im$\{\chi_1^1\}$.

time-dependent stimuli in high ac external fields are considered in the context of the Brownian motion of a particle in an external potential. For example, the approach presented can also be applied to the calculation of the dynamic Kerr effect ac response of *polar* and *anisotropically polarizable* molecules [6] and to the evaluation [28] of the nonlinear impedance of a microwave-driven Josephson junction [16,29] (as known, the dynamics of these systems is governed by very similar recurrence equations).

Note added in proof. Some time after this paper was sent for publication, Professor Yu. L. Raikher brought our attention to the publications [30,31], where the problem of the dynamic Kerr effect of *rigid* dipolar molecules in a strong ac electric field was treated by means of a numerical solution of Eq. (3) for $\xi_0=0$, which is the particular case of our problem. As is well known, the analysis of the measurements of the ac results of Refs. [30] and [31] [where the expectation value of the second Legendre polynomial $\langle P_2(\cos\vartheta)\rangle(t)$ was evaluated] may be considered to those obtained in the present paper. Furthermore, an analytical method, which was developed in [30,31] for the evaluation of the asymptotic behavior of the ac Kerr effect response in the high frequency ($\omega\tau_D \gg 1$) and strong ac field ($\xi \gg 1$) limits, can also be applied to the evaluation of the ac nonlinear dielectric response. In those limits, the reorientation of the particle is determined by the balance of viscous and field-induced torques as one may ignore the effects of the random torque acting on the particle. Thus, one may use the dynamic description for the rotation of the particle instead of the statistical one. In the context of this dynamic description, the behavior of the particle is governed by the following equation [30,31]:

$$\dot{\vartheta}(t) = -\frac{\xi\cos\omega t}{2\tau_D}\sin\vartheta(t),$$

which has an analytical solution

$$\cos\vartheta(t) = 2\left(1+\exp\left[-\frac{\xi}{\omega\tau_D}\sin\omega t\right]\tan^2\left[\frac{\vartheta(0)}{2}\right]\right)^{-1} - 1,$$

depending on the initial orientation of the particle $\vartheta(0)$. Assuming that at $t=0$ the particles were oriented randomly, we find, just as was done for $\langle P_2(\cos\vartheta)\rangle(t)$ in [30,31], a simple equation for $\langle\cos\vartheta\rangle(t)$ in Eq. (7), viz.,

$$\langle\cos\vartheta\rangle(t) = \coth z(t) - \frac{z(t)}{\sinh^2 z(t)},$$

where $z(t)=(\xi/2\omega\tau_D)/\sin\omega t$.

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